

# Superconductivity in $\text{Rh}_2\text{Ga}_9$ and $\text{Ir}_2\text{Ga}_9$ without Inversion Symmetry

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Superconductivity with  $T_c \simeq 2$  K was discovered in the intermetallic binary compounds  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ . This is the first observation of superconductivity in the Rh-Ga and Ir-Ga binary systems. Both compounds crystallize in a distorted  $\text{Co}_2\text{Al}_9$ -type structure (monoclinic, space group:  $Pc$ ), which lacks spatial inversion symmetry. Specific heat measurements revealed that both compounds are weak-coupling BCS superconductors having an isotropic superconducting gap. Measurements in magnetic fields indicated type-I superconductivity with a critical field  $H_c(0) \simeq 130$  Oe for  $\text{Rh}_2\text{Ga}_9$  and type-II superconductivity with an upper critical field  $H_{c2}(0) \simeq 250$  Oe for  $\text{Ir}_2\text{Ga}_9$ .

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Superconductors without spatial inversion symmetry have been attracting considerable interest. In such systems, if the antisymmetric spin-orbit coupling (SOC) is strong enough, a conventional classification of the pair wave function  $s$ -,  $p$ - or  $d$ -wave for the orbital part and singlet or triplet for the spin part is not valid anymore, and unconventional superconductivity with a nontrivial pair wave function is expected to appear [1, 2, 3]. Until now, superconductors without spacial inversion symmetry, and presumably having large SOC, have been discovered in compounds that consist of heavy transition metal ( $5d$ ), lanthanoid ( $4f$ ) and actinoid ( $5f$ ) elements. Among them,  $\text{CePt}_3\text{Si}$  [1],  $\text{UIr}$  [4],  $\text{CeRhSi}_3$  [5] and  $\text{CeIrSi}_3$  [6] constitute a family of heavy-fermion superconductors, and the nontrivial symmetry of Cooper pairs has been discussed in relation to the lack of inversion symmetry. Superconductivity in these systems, however, is located at the critical vicinity to the magnetic quantum critical point and coexists with antiferromagnetism or ferromagnetism. This can potentially make these compounds more fascinating; however, it may make the playground too complicated to capture the physics of inversion symmetry breaking and superconductivity.

In contrast, transition metal compounds with electron-phonon-mediated superconductivity give us an opportunity to investigate the bare effects of inversion symmetry breaking due to much weaker electron correlation for  $4d$  and  $5d$  systems. In addition, the magnitude of the SOC can be tuned by utilizing  $4d$  (small SOC) and  $5d$  (large SOC) elements in isoelectronic and isostructural compounds. Such an interesting case might be realized in the transition metal borides  $\text{Li}_2\text{Pd}_3\text{B}$  [7] and  $\text{Li}_2\text{Pt}_3\text{B}$  [8] in which the SOC for Pt ( $5d$ ) is much larger than that for Pd ( $4d$ ). The penetration depth [9] and  $^{11}\text{B}$  Knight shift [10] have suggested unconventional superconductivity with line nodes and significant spin-triplet component in pair wave function for  $\text{Li}_2\text{Pt}_3\text{B}$ , while conventional superconductivity with an isotropic gap for  $\text{Li}_2\text{Pd}_3\text{B}$ .

This motivated us to explore new superconductors

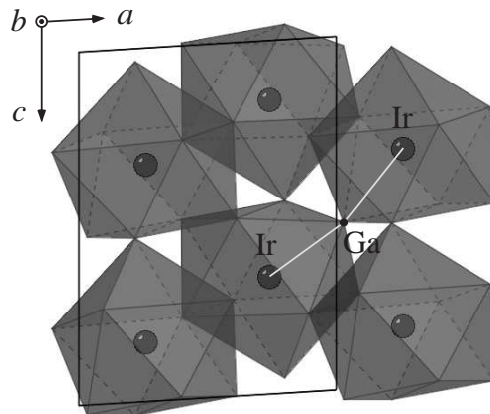


FIG. 1: Crystal structure of  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ . Monocapped square antiprisms  $[\text{IrGa}_9]$  with different orientations relative to  $[001]$  are stacked along  $[001]$  direction. The centering Ir atoms are represented by gray circles. The solid lines represent a monoclinic unit cell. White lines indicate a characteristic Ir-Ga-Ir bond, which determines the magnitude of the broken inversion symmetry (see text).

with  $4d$  and  $5d$  elements without spatial inversion symmetry. During the course of this study, we discovered superconductivity at about 2 K in the binary intermetallic compounds  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ . This is the first report on superconducting binary gallides containing Rh and Ir. In this Letter, we reveal their superconducting and normal state properties.

$\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$  crystallize in a monoclinic (distorted  $\text{Co}_2\text{Al}_9$ -type) structure with the space group  $Pc$  (No. 7), as shown in Fig. 1 [11]. The structure is characterized by a monocapped square antiprism centered at Ir (Rh). An Ir(Rh)-Ga-Ir(Rh) bond angle of  $165.8^\circ$  ( $164.5^\circ$ ) for  $\text{Ir}_2\text{Ga}_9$  ( $\text{Rh}_2\text{Ga}_9$ ) is much smaller than  $180^\circ$  and com-

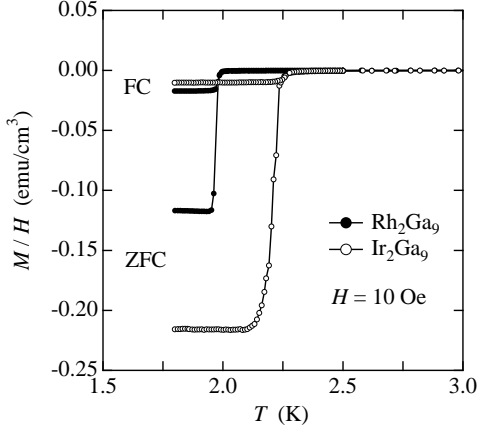


FIG. 2: Temperature dependence of the magnetization of  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ . The measurements were conducted in an applied field of  $H = 10$  Oe with zero-field-cooled (ZFC) and field-cooled (FC) processes.

parable with the Pt-B-Pt bond angle of  $150.1^\circ$  for antiperovskite  $\text{Li}_2\text{Pt}_3\text{B}$ . This ensures significant inversion symmetry breaking in  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ . Rhodium (4d) and particularly iridium (5d) are heavy elements, and the SOC should be invoked as an important ingredient for low-energy electronic states.

Polycrystalline samples were prepared by argon arc melting and subsequent heat treatment at  $500^\circ\text{C}$  under vacuum for one week. Powder X-ray diffraction measurements revealed the formation of  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$  without any noticeable impurity phases. The estimated lattice parameters were almost the same as reported in Ref. [11]. A low residual resistivity of  $\rho_0 \simeq 1 \mu\Omega\text{cm}$  and a large residual resistivity ratio (RRR) of  $\sim 150$  for both  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$  suggest high quality of the samples. Magnetic, transport and thermal measurements were conducted by using Magnetic Property Measurement System (MPMS, Quantum Design), Physical Property Measurement System (PPMS, Quantum Design) and  $^3\text{He}$  refrigerator (Heliox, Oxford).

The evidence for superconductivity in  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$  was found in the magnetization  $M(T)$  and electrical resistivity  $\rho(T)$ , as shown in Figs. 2 and 3(a), respectively. A large Meissner signal was clearly observed in the  $M(T)$  curve below  $T_c = 1.9$  and  $2.2$  K for  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ , respectively. Simultaneously, the  $\rho(T)$  exhibited a zero-resistive state. The field-cooled (FC) magnetization reached  $\sim 20\%$  of the perfect diamagnetism at low temperatures. This large Meissner effect is the hallmark of bulk superconductivity.

Further support for bulk superconductivity was obtained from the specific heat  $C_p(T)$ , where a clear jump at the superconducting transition was observed, as shown in Fig. 4. In order to accurately determine bulk  $T_c$  in zero magnetic field, an idealized jump at  $T_c$  was assumed

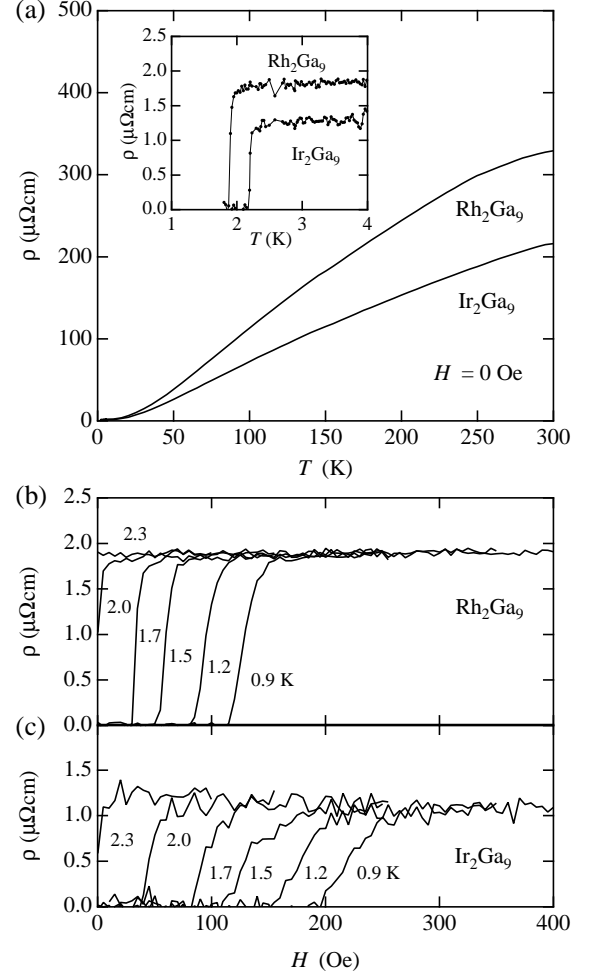


FIG. 3: (a) Temperature dependence of electrical resistivity  $\rho$  of  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$  in zero applied field. (b) and (c) Low-temperature resistivity as a function of magnetic field  $H$ . The measurements were conducted on decreasing  $H$  ( $\parallel j$ : current) from the normal state at constant temperatures (0.9, 1.2, 1.5, 1.7, 2.0 and 2.3 K) with a sufficiently low current density of  $\sim 0.5 \text{ A/cm}^2$ .

to satisfy the entropy conservation at the transition. This yielded an estimate of  $T_c = 1.9$  and  $2.2$  K and  $\Delta C_p/T_c = 11.3$  and  $9.8 \text{ mJ/K}^2\text{mol}$  for  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ , respectively. A standard analysis yielded the normal-state  $T$ -linear specific heat coefficient  $\gamma_n = 7.9$  and  $6.9 \text{ mJ/K}^2\text{mol}$  and Debye temperature  $\Theta_D = 312$  and  $264$  K for  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ , respectively. By using these values, we estimated  $\Delta C_p/\gamma_n T_c \simeq 1.4$  for both  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ , which is almost identical to the value expected from the BCS weak-coupling limit ( $\Delta C_p/\gamma_n T_c = 1.43$ ). In zero applied field,  $C_p(T)$  showed exponential temperature dependence at low temperatures. Indeed, the  $C_p(T)$  data can be fitted reasonably by those expected from the weak-coupling BCS theory (represented by solid lines in Fig. 4) [12]. All of these results suggest that both

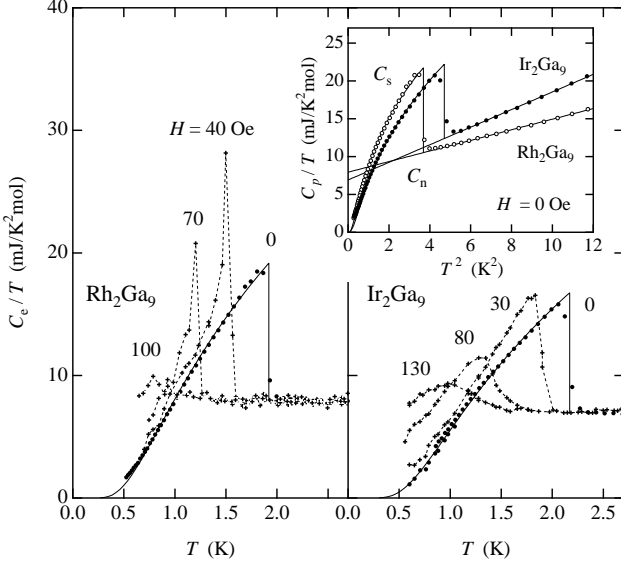


FIG. 4: Electronic specific heat divided by temperature  $C_e/T$  as a function of temperature  $T$  in various magnetic fields for  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ . Solid lines for the  $H = 0$  data represent  $C_e/T$  expected from the weak-coupling BCS theory [12]. The inset shows specific heat divided by temperature  $C_p/T$  as a function of  $T^2$  in zero applied field. The solid lines represent a fit to  $C_n/T = \gamma_n + \beta T^2$ .

$\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$  are weak-coupling superconductors with an isotropic superconducting gap.

Although the zero-field specific heat data were similar, the behavior in magnetic fields was distinctly different between  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ . This can be clearly seen in Fig. 4.  $\text{Rh}_2\text{Ga}_9$  exhibited a divergent  $C_p(T)$  anomaly at the transition, the characteristic of a first-order transition, when  $H \neq 0$ . This strongly suggests that  $\text{Rh}_2\text{Ga}_9$  is a type-I superconductor and that the superconducting transition becomes a first-order transition in magnetic fields. As shown in Fig. 5, the  $H_c - T_c$  curve, obtained from the specific heat anomaly, agreed very well with the thermodynamic critical field  $H_c(T)$ , which was estimated from the free-energy difference in zero applied field:  $\Delta F(T) = F_n - F_s = H_c^2(T)/8\pi = \int_T^{T_c} \int_{T'}^{T_c} (C_n/T'' - C_s/T'') dT'' dT'$ . Here, we used the zero-field specific heat data for  $C_s$  and assumed  $C_n = \gamma_n T + \beta T^3$  (see the inset in Fig. 4). This, together with the first-order transition in  $H$ , indicates that  $\text{Rh}_2\text{Ga}_9$  is a type-I superconductor with a critical field of  $H_c(T=0) \simeq 130$  Oe. In contrast, the specific heat of  $\text{Ir}_2\text{Ga}_9$  exhibited a second-order behavior at  $T_c$  in  $H$ . The observed  $H_{c2} - T_c$  curve is located at a higher field than the thermodynamic critical field  $H_c(T)$ , suggesting type-II superconductivity in  $\text{Ir}_2\text{Ga}_9$ . We estimate a coherence length of  $\xi \sim 1000$  Å from the linearly extrapolated upper critical field  $H_{c2}(0) \simeq 250$  Oe. Frigeri *et al.* predicted that

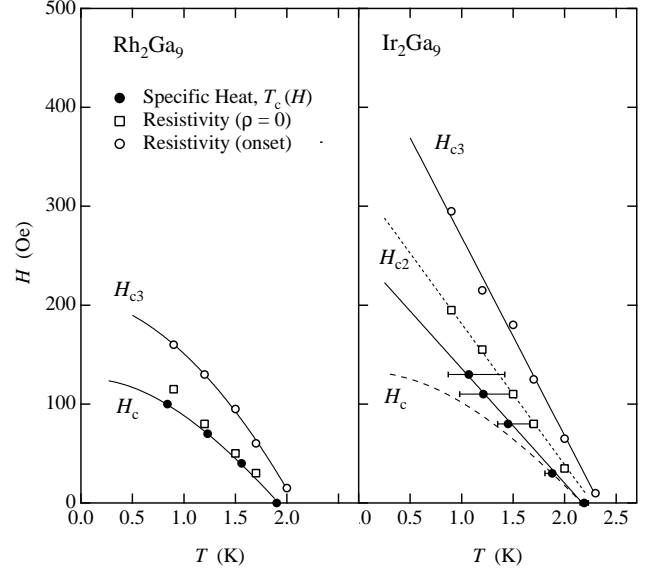


FIG. 5: Magnetic field ( $H$ ) versus temperature ( $T$ ) phase diagram of  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ . Filled circles and open squares represent the superconducting transition temperatures determined by specific heat and resistivity, respectively. Open squares represent the onset magnetic field of surface superconductivity. Thermodynamic critical field  $H_c(T)$ , determined from the zero-field specific heat, is shown by solid and broken lines for  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ , respectively.

if the spin-triplet component is present due to an antisymmetric SOC, the paramagnetic limiting field  $H_P$  is enhanced from the value without the SOC,  $H_P^0 \simeq 1.85T_c$  (in Tesla) [2, 3]. However, because of the long coherence length and the resultant much lower orbital limiting field ( $\simeq 250$  Oe) than  $H_P^0 \simeq 3.7$  T (expected from  $T_c = 2.2$  K for  $\text{Ir}_2\text{Ga}_9$ ), we were not able to examine if  $H_P$  is enhanced and the effect of the antisymmetric SOC is noticeably large in  $\text{Ir}_2\text{Ga}_9$ .

The long coherence length  $\xi$  of the present compounds gives rise to surface superconductivity: when we have a flat plate of a superconductor, with the applied magnetic field parallel to the flat surfaces, superconductivity can exist in the surface layers with a thickness of coherence length, while the bulk region inside of the sample has a zero order parameter [13]. Figures 3(b) and (c) show the resistivity  $\rho$  as a function of  $H$  for  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ , respectively. The magnetic field  $H$  was applied parallel to the current direction and sample surfaces with a parallelepiped shape. Zero resistivity persisted in the bulk superconducting state up to the critical field  $H_c(T)$  for type-I  $\text{Rh}_2\text{Ga}_9$  and the upper critical field  $H_{c2}(T)$  for type-II  $\text{Ir}_2\text{Ga}_9$ . Even above  $H_c(T)$  or  $H_{c2}(T)$ ,  $\rho(H)$  was still smaller than the normal-state value and gradually increased until  $\rho(H)$  reached to the value in the normal state at the surface critical field  $H_{c3}(T)$ . The estimated  $H_{c3}(T)$ , together with  $H_c(T)$  and  $H_{c2}(H)$ , are shown in

Fig. 5. By using the relation  $H_{c3} = 1.7\sqrt{2}\kappa H_c$  [13], we estimate a Ginzburg-Landau parameter  $\kappa \simeq 0.7$  and 1.1 for  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ , respectively. The latter agrees reasonably with  $\kappa = H_{c2}/\sqrt{2}H_c \sim 1.3$ . These  $\kappa$  values indicate that  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$  are located near the boundary of type-I and type-II superconductivity with  $\kappa = 1/\sqrt{2}$ .

The observed electronic specific heat coefficient  $\gamma_n = 6.9 \text{ mJ/K}^2\text{mol}$  for  $\text{Ir}_2\text{Ga}_9$  is only slightly enhanced as compared to that obtained from the band calculation  $\gamma_{\text{band}} = 5.9 \text{ mJ/K}^2\text{mol}$  [11]. This yields an electron-phonon coupling constant of  $\lambda_{\text{ep}} \sim 0.17$  assuming  $\gamma_n = (1 + \lambda_{\text{ep}})\gamma_{\text{band}}$ , which is consistent with the weak-coupling limit inferred from the specific heat jump  $\Delta C_p/\gamma_n T_c$ . We believe that the same is true for  $\text{Rh}_2\text{Ga}_9$ . The rather small enhancement of  $\gamma_n$  as compared to  $\gamma_{\text{band}}$  probably indicates that the correlation effect is not significant. The  $\gamma_n$  value of  $7 - 8 \text{ mJ/K}^2\text{mol}$  at first glance does not appear to be so small. The band calculation indicates that the electronic state at the Fermi level  $E_F$  is primarily of the Ga  $4s$  and  $4p$  character [11]. It is, therefore, more practical to rewrite  $\gamma_n$  as  $\simeq 0.84 \text{ mJ/K}^2\text{mol-Ga}$  for  $\text{Rh}_2\text{Ga}_9$  and  $\simeq 0.77 \text{ mJ/K}^2\text{mol-Ga}$  for  $\text{Ir}_2\text{Ga}_9$ . It is clear that these systems have a low electronic density of states at  $E_F$ . In accord with this, the magnetic susceptibility of these compounds in the normal state was diamagnetic,  $\chi \simeq -2.7 \times 10^{-4} \text{ emu/mol}$  for  $\text{Rh}_2\text{Ga}_9$  and  $\simeq -3.0 \times 10^{-4} \text{ emu/mol}$  for  $\text{Ir}_2\text{Ga}_9$ . The small contribution from Rh and Ir to the electronic states near  $E_F$ , as inferred from the band calculation of  $\text{Ir}_2\text{Ga}_9$ , partly explains the absence of a noticeable SOC effect in both  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$  and the conventional behavior of superconductivity. Another point to be noted is that even for  $\text{Ir}_2\text{Ga}_9$ , the strength of the SOC  $\alpha_{\text{SO}} \sim 200 \text{ meV}$  is much smaller than the Fermi energy  $E_F$  ( $\sim 12 \text{ eV}$ ) [11]. Frigeri *et al.* predicted that if  $E_F \gg \alpha_{\text{SO}}$ , the mixing of the spin-singlet and spin-triplet states is negligibly small and  $T_c$  of the spin-singlet state is essentially unchanged by introducing the antisymmetric SOC [2, 3]. Thus, the almost same  $T_c$  of  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$  suggests a dominant singlet component in the pair wave function of  $\text{Ir}_2\text{Ga}_9$ . In contrast with  $\text{Ir}_2\text{Ga}_9$ ,  $\text{Li}_2\text{Pt}_3\text{B}$  has the conduction band with a predominantly Pt  $5d$  character and a clear decrease in  $T_c$  as compared to  $\text{Li}_2\text{Pd}_3\text{B}$ , as well as the signature of unconventional superconductivity, was observed. It is still not clear, however, whether  $\alpha_{\text{SO}}$  can be of the order of  $E_F$  in  $\text{Li}_2\text{Pt}_3\text{B}$ .

In conclusion, by exploring group 9 transition metals (Co, Rh and Ir) and Ga binary systems, we discovered new superconductors  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$  with  $T_c = 1.9$  and  $2.2 \text{ K}$ , respectively.  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$  are the first examples of superconductors in the Rh-Ga and Ir-Ga binary systems. The superconducting and normal state parameters, as summarized in Table I, revealed that  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$  are weak-coupling BCS superconductors with an isotropic superconducting gap.

TABLE I: Superconducting and normal state parameters for  $\text{Rh}_2\text{Ga}_9$  and  $\text{Ir}_2\text{Ga}_9$ .

	$\text{Rh}_2\text{Ga}_9$	$\text{Ir}_2\text{Ga}_9$
Transition temperature, $T_c$ (K)	1.9	2.2
$T$ -linear coefficient, $\gamma_n$ (mJ/K <sup>2</sup> mol)	7.9	6.9
Debye temperature, $\Theta_D$ (K)	312	264
$\Delta C_p/\gamma_n T_c$	1.4	1.4
Thermodynamic critical field, $H_c(0)$ (Oe)	126	133
Critical field, $H_c(0)$ (Oe)	$\simeq 130$	n.a.
Upper critical field, $H_{c2}$ (Oe)	n.a.	$\simeq 250$
Ginzburg-Landau parameter, $\kappa$	$\simeq 0.7$	$\simeq 1.1$

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*Note added.* — Wakui *et al.* [16] have recently reported superconductivity in the same compounds [17].

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